Hydration and Strength of Cement and Concrete.
By A. J. EIGER

THE strength of hardening cement is due to the shrinkage of a gel formed by the action of water on cement. This strength depends on the fineness of grinding and on the chemical properties of the cement. Knowing the dimension of a cement particle and the speed with which water penetrates it during a known time, we may easily calculate the rate of its hydration and thus obtain an idea of the quantity of gel formed.

The determination of particle size and of the quantity of particles of every average size in a cement can be made by means of any elutriation method. The determination of the rate of hydration is far more complicated. A method
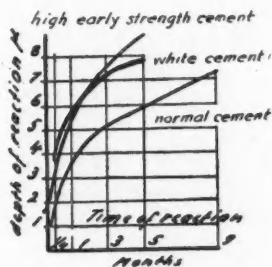
Fig. 1.

based on different optical properties of hydrated and unhydrated cement has been worked out by Anderegg and Hubbel, who were the first to show the progress of hydrating reactions on different cements by plotting as ordinates the thickness of the hydrated layer on the examined particle and as abscissæ the time of hydration. Fig. 1 gives the original curves.

If we know the granulometric composition of a cement and its hydration

rate we can proceed as follows.   If the finest fraction of a cement has 5 gr. between 0 and 2 microns., 5 gr. between 2 and 4, and 10 gr. between 4 and 8 microns, we can substitute for these fractions their average dimension and define the cement as containing 5 gr. cubic particles of 1 micron, 5 gr. of 3 microns, and 10 gr. of 6 microns.   It can be shown that the error in this method is not important.

The curve shows that after one day the hydration reached a depth of 0·5 micron.   Thus the one micron fraction was not present, the particles of the next fraction measured two microns, and the largest fraction measured five instead of six microns.

We can write

	Unhydrated.		Hydrated.		
Fraction.	Average size.	gr.		gr.	Per cent.
0—2	1	5	$\dfrac{3^3-2^3}{3^3} \times 5$	5	100.0
2—4	3	5		3.15	63.0
4—8	6	10	$6^3-5^3 \times 5$	2.11	21.1
		20	6^3	10.26	

total hydration rate of this fraction $=$

$$\frac{10.26}{20} = 51.3 \text{ per cent.}$$

It is interesting to note how slight is the hydration of greater particles in the same time.   For instance, for a particle of sixteen microns we get after one day

$$\frac{16^3-15^3}{16^3} = 1\cdot77 \text{ per cent.}$$

Similarly we may calculate this rate for any period of hardening.   This method, though affected by the approximation of the assumed uniform content of cubic particles of average size in any separated fraction, presents also the possibility of determining in a similar way the inner surface of a cement, and what is more important, the changes occurring in this value during the hydration process.

Anderegg and Hubbel's method is ingenious but difficult.   The author has evolved another method based on the fact that hydrated cement has a specific gravity of 2·13.   If we consider a cement, having a specific gravity of 3·13, which after a certain hydration period is reduced to 2·63, it is calculable that this cement is hydrated up to 50 per cent.   When it is desired to find the hydration rate of a cement in the most important periods, and also to generalise this data for the same clinker of any fineness, we must proceed in the inverse way.   Knowing the granulometric composition of the cement we assume that its reaction is according to a curve, and this is easy to agree by analogy with similar cements.   On this basis we calculate the total hydration rate at different ages and compare the results with those experimentally obtained.   If the calculated hydration is higher after three days but smaller after twenty-eight days than the experi-

mental determination, it is clear that the hydration curve has been plotted too high in the first case but too low in the second case. As a rule after one correction the curve checks with the experimental results. The ultimate results may be checked by repeating this operation on a specimen of the same clinker differently ground. The determination of specific gravity is a simple operation and the errors of experiment and calculation are smaller than those in the Anderegg method. For this reason it is considered more suitable for practical purposes.

In this way the author has determined the rate of hydration of three cements of which the chemical analyses are given in Table I ; W is a good rapid-hardening Portland cement, S a Kühl cement, K a shaft-kiln cement. The hydration rates
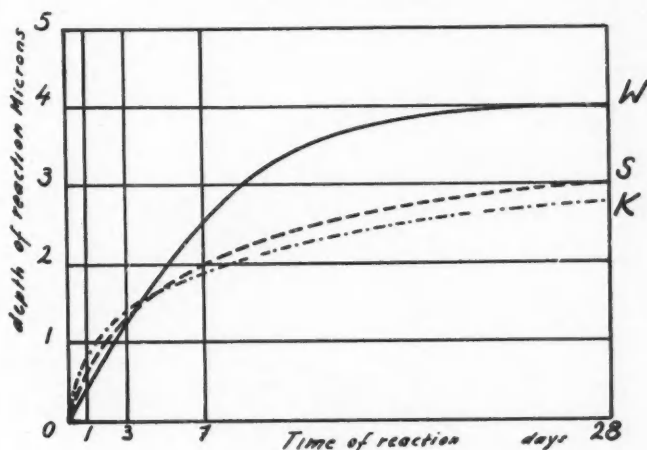

Fig. 2.

are shown on Fig. 2. In the case of cement W, after one day all particles of one micron disappeared, after seven days all up to five microns, after twenty-eight days all up to eight microns. This result is checked by another experiment. Fig. 3 shows the granulometric composition of a clinker ground in a tube mill and Fig. 4 the strength of the same specimens. The abscissæ are the corresponding inner surfaces. Comparing these two figures we see that the increase of strength after seven and twenty-eight days ceases after reaching the abscissæ 2,150, while the fraction 0–4 microns increases further from 10 to 25 per cent. and the fraction 4–8 microns from 25 to 45 per cent. Considering that an increase of strength can only proceed when new quantities of clinker are entering into reaction, and these quantities consist almost entirely of particles below eight microns, larger particles are playing only a small part and particles of the respective sizes of 0–4 or 4–8 microns practically do not exist after seven and twenty-eight days.

Another fact confirmed by Figs. 3 and 4 is that grinding beyond a certain limit does not result in further increase in strength, especially after twenty-eight

days. The decrease found by Kühl[1] has not been confirmed because his tests were made not on the basis of a constant water addition but on the basis of the same consistency. As the more finely ground cement requires more mixing water to give similar strength, the result was naturally a decrease.

TABLE I.

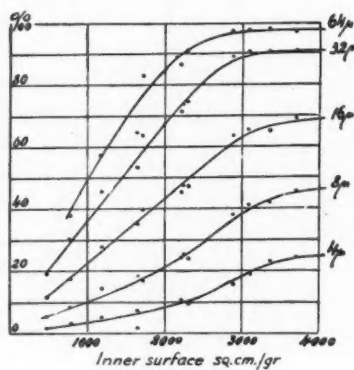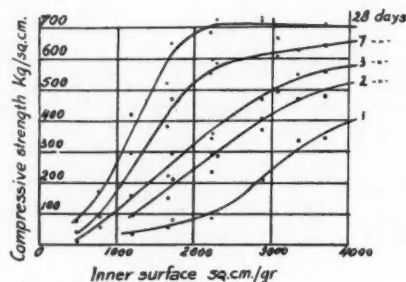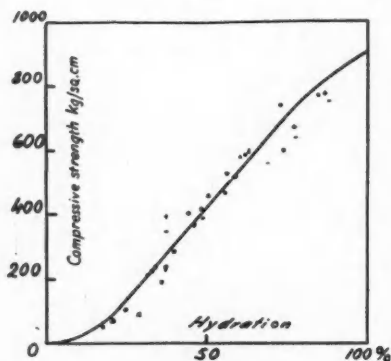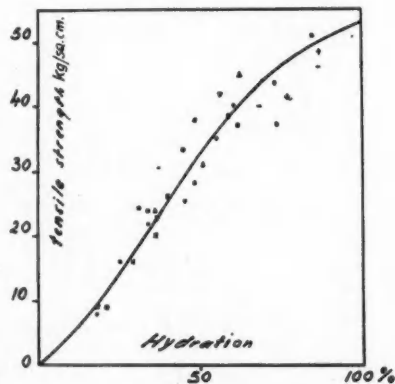|	Portland cement.	Kühl cement.	Shaft kiln cement.
SiO_2	21·4	17·5	19·7
Al_2O_3	6·3	8·7	5·8
Fe_2O_3	2·6	4·7	4·0
CaO	66·0	63·6	65·3
SO_3	1·25	2·4	1·5
MgO	1·3	1·2	1·3
Ignition	0·9	1·5	1·9

Fig. 3.

Fig. 4.

Fig. 5.

Fig. 6.

[1] Kühl, *Zement*, 1929, 1930.

The relation between the compressive and tensile strengths of standard 1:3 mortar as a function of hydration is shown in Figs. 5 and 6.   It is interesting to note that data obtained from different cements at different ages are almost on the same curve.   This confirms the suggestion that the hardening of every Portland cement is caused by the same active component, the content of which is a measure of the quality of the cement.   The strengths of coarsely-ground cements were too small to give appreciable results when tested as standard mortar.   They were repeated with 1 : 2 mortar, and after a proportional correction they checked with the same curve.

The compressive strength curve can in its middle course be substituted by a straight line ; this is why the compressive strengths of concrete are also proportional to the strength as well as to the quantity of cement.   The curves representing the relation of concrete strength to cement quantity as plotted by Kortlang and Suensson have exactly the same shape as those in Fig. 5.   The relation given by Féret between compressive and tensile strengths is also confirmed by these curves.
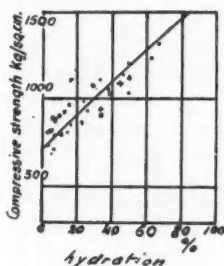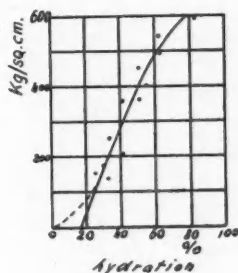
Fig. 7.   Fig. 8.

It will be realised from the foregoing that hardened neat cement is an agglomeration of particles of unhydrated clinker located in a hydraulic gel.   It represents a mortar of which the unhydrated cores of the particles are the aggregate.   Thus all laws applying to mortar and concrete are relevant to neat hydrated cement ; for example, hydrated and re-ground cement must behave as a cement containing so many active parts as were unaffected by the first hydration.   The same relation must exist between the original and the second strengths.

To confirm this the author made a series of tests[2] as follows.   Four cements obtained by different grinding of the same clinker were hydrated with 25 per cent. water and after respectively one, three, seven and twenty-eight days were re-ground to a residue of nil on a sieve of 10,000 meshes per sq. cm.   These " new " cements were pressed with 15 per cent. water at a pressure of 400 kg. per square centimetre in cylinders of 30 mm. diameter and height.   Another series of cylinders was obtained by the addition to one part of new cement, two parts of standard sand, and 33 per cent. water and both series were tested after three, seven and

² *Zement*, 1932.

twenty-eight days of hardening. The strengths were plotted against the hydration rate, which was calculated as follows: taking K_1 as the hydration rate at one day and K_7 as the hydration rate after seven days, the hydration rate of such a cement re-ground after one day hydration and tested after seven further days is

$$K = \frac{100 - K_1}{100} \times K_7$$

In the inverse case, when the cement was tested at one day, being re-ground after seven days' hydration,

$$K = \frac{100 - K_7}{100} \times K_1$$

Figs. 7 and 8 were thus obtained, Fig. 7 by crushing samples of mixes from " new " re-ground cement and " old " hardened cement two years old and
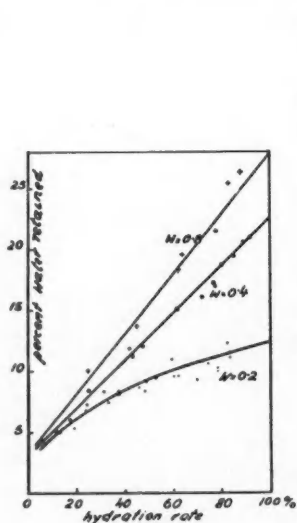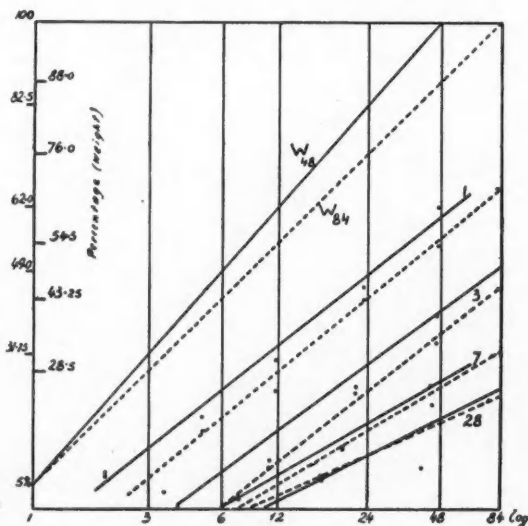
Fig. 9a.   Fig. 9b.

assumed to have the same properties as the hydrated gel in proportions varying from $1:\frac{1}{4}$ to $1:10$ and Fig. 8 by adding standard sand to " new " re-ground cement in the same proportions. In both cases the hydration rate was calculated as before. The curve on Fig. 8 is similar to the curve on Fig. 5, which fully agrees with our suppositions. Fig. 7 shows that there is a certain amount of strength when the hydration is equal to zero. This amount corresponds to the strength of the hardening products in the re-ground gel.

Another possible source of error is the fact that the secondary grinding may give different granulations and therefore different strengths. This was eliminated by grinding the hardened cement so as to reach the region where, according to

Figs. 3 and 4, the fineness has no more influence on strength.[3]   We have thus been able to determine the quantity of " active " cement that enters into the hardening process as well as the law that governs the corresponding strength. The difficulties of defining the ways in which water is contained in hardening Portland cement has been often discussed without satisfactory results. The author started by repeating the tests of Werk and Lasseter in drying at 100 deg. C. and then heating the cements, to which 10, 20, 40 and 80 per cent. of water were added at ages of one, three, seven and twenty-eight days respectively. The results obtained by the former tests were confirmed.   Fig. 9a shows the amounts of water remaining after drying plotted against the corresponding hydrations.   It shows a direct proportion, while the water residue increases with increasing water ratio.   The first fact demonstrates that as water is, apart from
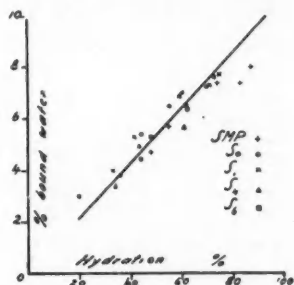
Fig. 10.

chemical binding, kept in the gel by adsorption and capillary attraction its quantity can be greater when there is a greater amount of gel, or in other words, a greater hydration.   The second can perhaps be explained by stating that, in the case of a large water ratio, all the capillary channels are enlarged and the heat transmission from their walls (proportional to the surfaces) has to evaporate a larger amount of water than in the case of smaller ratios.

The author attempted to discover what quantities of water cannot be removed by heating up to 300 deg. C.   By testing the three cements of Table I he found the line plotted on Fig. 10.   By extrapolation it would give 11 per cent. as the amount of chemically bound water, while investigations of Hart and Otzen show 13 per cent.   The author is inclined to think that 11 per cent. is rather too little.   At 300 deg. C. the $Ca(OH)_2$ contained in hydrated cement loses part of its combined water, so that the quantity of water remaining is less by this amount. The two points on Fig. 10 corresponding to the maximum hydration, and therefore to the highest $Ca(OH)_2$ content, present a clear indication on this point.   Con-

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[3] Another illustration of the relationship between neat cement paste and mortar or concrete may be seen from following: Professor Anderegg found that those cements give the greatest neat strengths which are ground to a logarithmic granulation.   If now we calculate the grading of the cement particles after any time, its unhydrated remainder will always agree closely to a logarithmic curve, being thus simply but a mortar with graded aggregate which is known to give the greatest strength.

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sidering that a temperature of 300 deg. C. is as well or as little justified as, say, 270 deg. or 280 deg. C., the result of 11 per cent. is considered merely as an indication. In any case from both Figs. 9 and 10 it is obvious that this ratio lies beyond 10 per cent.

What happens to the great excess of water used in practice ? Most of the cements used rarely hydrate more than up to 70 per cent. Therefore the water bound in a chemical way and by adsorption, etc., cannot exceed 14 to 16 per cent. The absorption of aggregate can add a little to this, but the total is very small when we realise that practical water-cement-ratios range from 40 to 100 per cent. Evaporation during hardening is prevented, and so the excess of water is kept in the hard mass for a long time, but ultimately it is drawn to the surface by capillary forces and then leaves voids. It has the same influence on concrete as gas from aluminium powder has on cellular concrete. Fig. 11 shows the results
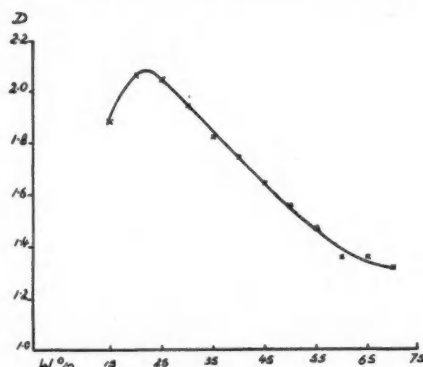
Fig. 11.

obtained by Dr. Hummel on cubes of neat cement with various water-cement-ratios. After the ratio 0.2 the volume of voids increases rapidly, diminishing the specific gravity. It has been suggested that the strength decrease due to the use of greater water ratios is due to a secondary hydrolysis which occurs in the hardened cement, thus affecting its strength. The reply is that the only known fact in this connection is the solubility of CaO in water in the proportion of 2 gr. to one litre, which means an exaggerated water ratio of 50,000 per cent. On the other hand Kühl showed that a saturated solution of $Ca(OH)_2$ cannot hydrolise hardening cement. If we test the water during hardening at different moments we find, according to Fig. 12, that it is saturated after a very short time. Therefore the only influence of the water ratio on the strength of cement or concrete is due to the increase of voids its causes.

It seemed to be important to ascertain the relation between the volume of voids and the strength of a cement paste. This relation is the basis of the well-known concrete strength determinations of Talbot, Richard and Féret. The

compressive strength was measured by crushing standard cubes of 7·09 cm. side of neat cement, to which 25, 40, 60 and 80 per cent. water were added. From the same paste plates 7·09 by 7·09 by 1 cm. were formed and the volume of voids measured in the three following ways: (1) The plates were dried in a stream of air of 30 deg. C. and kept for twenty-four hours in a dessicator; (2) the plates were dried by heating to 110 deg. C., and (3) the plates were finely ground and the specific gravity found by means of a picnometer. Knowing the total volume, the voids were easily calculated.
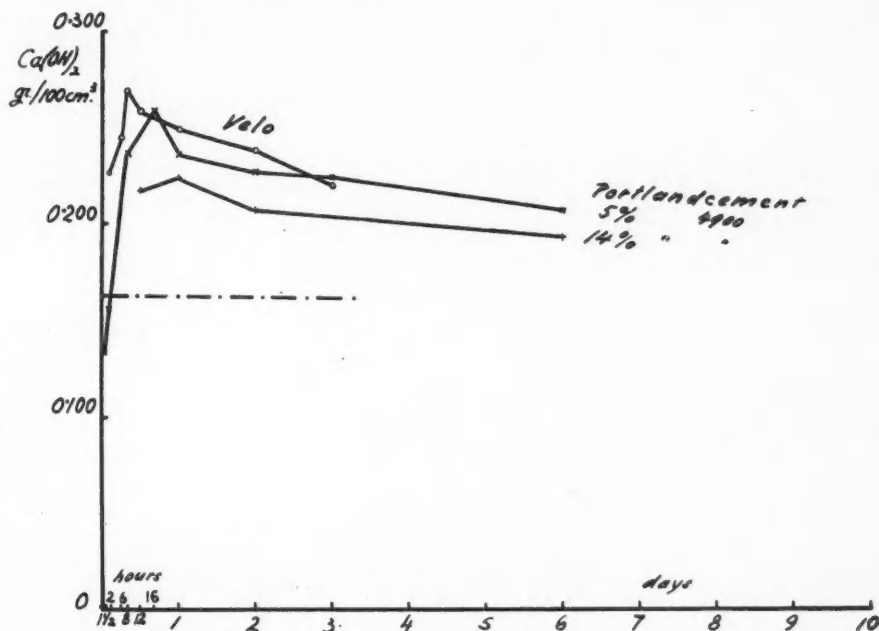
Fig. 12.

These tests were made for the three cements mentioned, and the results are plotted on Fig. 13 and follow with great approximation the formula

$$F = \frac{A}{b \dfrac{V_0}{V - V_0}}$$

where F is the crushing strength, A and b constants, V the total and V_0 the voids volume. In this case A represents the value of F when $V_0 = 0$, and consequently the denominator becomes equal to 1. As we can see by extrapolation this value is about 2,000 kg. per sq. cm. The Swedish investigations of Stig-Hedström gave for this a result of 1,600 kg. per sq. cm., while Anderegg reports 2,660 kg. per sq. cm. The results are so different because in each case different

samples were crushed, and the influence on the test result of form and dimension is very important.

We can easily find the relation between voids, volume, water ratio, and hydration : Let V be the total volume, V_0 the volume of voids, W the volume of water, C the volume of cement by weight, H the hydration rate in per cent., 12 per cent. the amount of water chemically bound, and 3·15 and 2·13 the specific gravities of unhydrated and hydrated cement, then

$$V_0 = \frac{c}{3·15} + W - \frac{H \times c \times 1.12}{2·13} - \frac{(1 - H)c}{3·15} = W - 0·21 \, H.C.$$

$$V - V_0 = \frac{c}{3·15} + W - W - 0·21 \, H.C = C(0·32 + 0·21H)$$

$$\frac{V_0}{V - V_0} = \frac{W - 0·21 \times H \times C}{C(0·32 + 0·21H)} \text{ or putting } \frac{W}{C} = X, \frac{V_0}{V - V_0} = X$$

$$= X \frac{1}{0·32 + 0·21H} - \frac{0·21H}{0·32 + 0·21H}$$

It is interesting to note that the formula for neat cement gel has the same form as the well known formula of Abrams for the strength of concrete, but in this case the water-ratio X is affected by a correction factor which takes account of the water needed for hydration.
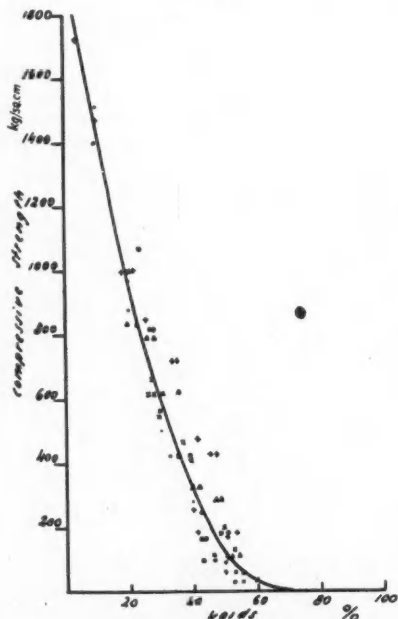
Fig. 13.
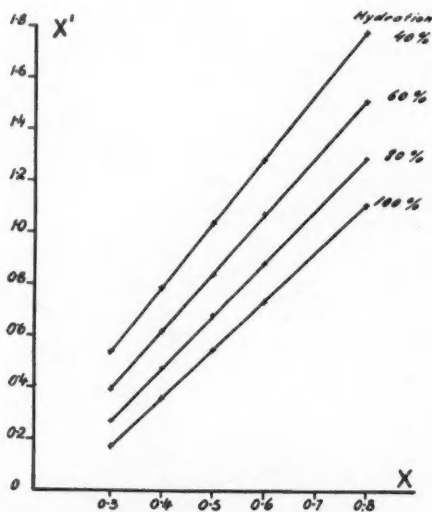
Fig. 14.

If we consider Abrams' formula in the original form $F = \dfrac{1,000}{B^x}$ we must say that it has not a logical interpretation. It is obvious that the crushing strength of a cement, mortar, or concrete will be at its highest limit when there are no voids in it, when V_0 equals zero. If we would apply these considerations to the Abrams' formula, we see that this highest limit occurs when $B^x = 1$ or $\dfrac{W}{C} = X = 0$. But the former condition can be realised only when $W = C$ which means that maximum strength can be obtained without hydrating the cement !

In our formula we get the minimum voids when $\dfrac{W}{C} = 0.21$, which agrees with Fig. 11. The value of X' is shown on Fig. 14 as function of X for a coarse ($H = 40$ per cent.), normal ($H = 60$ per cent.), and a finely ground (80 per cent.) cement after twenty-eight days of hardening. The differences between X and X' are in some cases very important.

It is easy now to calculate the volume of voids in all the cases described before and plotted on Fig. 13. As we see from Table II, they agree with the previous results and confirm also all our results or suppositions concerning the rate of hydration and percentage of bound water. The volumes of voids found by heating to 110 deg. C. are larger than those determined by the picnometer method ; this is due to the shrinkage occurring in the hydrated gel when dried, which enlarged the voids. The relative greater discrepancy between the results after seven and twenty-eight days with $W = 0.25$ are due to the greater influence of a probably constant experimental error on smaller absolute values.

TABLE II.

VOLUMES of VOIDS.

Type of Cement.		$\dfrac{W}{C}$	3 days.			7 days.			28 days.		
			Dried at 110 deg. C.	Picnometer. (110 deg.C.)	Calculated.	Dried at 110 deg. C.	Picnometer. (110 deg.C.)	Calculated.	Dried at 110 deg. C.	Picnometer. (110 deg.C.)	Calculated.
Kühl		0·25	25·2	25·0	24·2	—	—	—	21·7	21·5	17·9
		0·4	41·5	38·2	40·1	—	—	—	33·5	31·1	35·0
		0·6	54·1	49·5	50·2	—	—	—	47·2	43·8	45·8
Shaft kiln ..		0·25	27·8	26·0	26·1	27·5	25·2	21·8	27·5	24·4	20·6
		0·4	39·4	36·9	39·8	37·4	34·3	36·9	37·0	32·8	35·8
		0·6	52·5	49·4	53·5	49·6	46·7	50·3	49·5	45·1	49·0
Rotary	I. ..	0·25	32·8	—	32·2	27·7	—	26·6	—	—	—
		0·4	46·7	—	43·7	42·8	—	39·0	—	—	—
		0·6	55·3	—	52·7	50·3	—	46·5	—	—	—
Kiln	II. ..	0·25	30·0	—	30·2	23·4	—	—	—	—	—
		0·4	43·5	—	42·7	39·1	—	37·7	—	—	—
		0·6	55·2	—	53·0	51·0	—	48·7	—	—	—
W.	III. ..	0·25	28·1	—	26·0	23·4	—	19·3	—	—	—
		0·4	42·2	—	40·0	35·7	—	35·0	—	—	—
		0·6	54·5	—	52·0	48·3	—	47·4	—	—	—

To generalise the validity of our formula for any mix it is necessary to consider different cement contents. It is obvious that if we compare two concretes or mortars with the same content their strengths will be proportional to their respective hydration rates.

As we see from Fig. 5 (on its straight-line part) there must be a certain amount of cement already hydrated to obtain any visible strength. This amount is, according to Figs. 5 and 6, about 13 to 14 per cent. Stig-Hedström found this amount to be 25 per cent. by volume.

In the same way as above we find 14 per cent. by weight to be

$$\frac{14 \times 1\cdot12 \times 3\cdot15}{2\cdot13} = 23\cdot7 \text{ per cent. by volume, or practically the same.}$$

The formula becomes, for a given standard mix, say 350 kg. of cement per cubic metre of concrete,

$$K = \frac{A(h-13)}{b^{x'}}$$

and for any other mix containing c kg. cement for a cubic metre of concrete

$$K_a = \frac{A(h-13)}{b^{x'}} \frac{c}{350}$$

We put $h-13$ as the proportionality factor because in this case we do not use the complete curve on Fig. 5, but its straight-line part on which all commercially ground cements can be plotted. It is obvious that for $H-13$ the strength is zero. To verify this formula a series of tests was made with a concrete containing 350 kg. of cement per cubic metre, $\frac{W}{C}$ being 0·4, 0·6 and 0·8. The aggregate was of the same grading for all tests, and differently ground clinkers of all the three kinds were used. The samples were 10 cm. cubes. Table III gives the results, which agree with the formula.

TABLE III.

Type of cement.	Cement content kg. per cubic centimetre.	$\frac{W}{C}$	b 7 days.	b 28 days.
Kühl S.	350	0·4 0·5 0·6	5·41 5·79 5·17	4·98 4·65 5·07
Shaft kiln K.	350	0·4 0·5 0·6	4·88 4·92 5·15	4·78 4·85 5·12
Rotary kiln I.	350	0·45 0·55	5·11 5·10	— —
W. II.	450	0·35 0·45 0·55	5·8 5·3 5·3	— — —

This formula can be physically interpreted as follows. The strength of any mortar or concrete cannot be greater than a certain figure, being the " technical
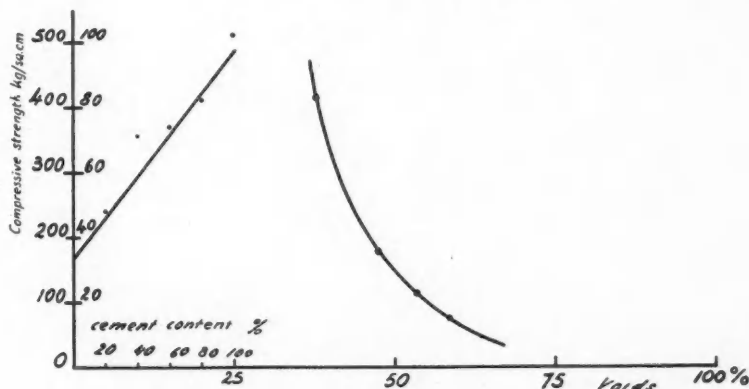
Fig. 15.

value " of the molecular strength of cement gel. It is affected positively by the concentration of cement in the mortar and negatively by the effect of voids, these factors being expressed respectively by the numerator and the denominator of the formula, while b is a constant depending on the sample form. This rule is of a general kind concerning rigid and amorphous matter.

Even if we go as far as the field of cellular concretes the same factors, namely, concentration and voids, provide the same effects as are seen on Fig. 15.

When compared with other known formulæ the function represents always their general form. Let us consider the Graf formula for the compressive strength of concrete

$$K = \frac{Kn}{400}\left(\frac{1640}{72_w} + 30\right)$$

where Kn is the standard tests compressive strength, $_w$ the water-cement-ratio by weight, 400 the average standard strength after twenty-eight days. For practical water-cement-ratios we may write :

$$K = \frac{1{,}850 - 2{,}800}{72_w} \times \frac{Kn}{400}.$$

We have seen from Fig. 14 that, especially with coarsely-ground cement, the effect of hydration rate doubles the exponent so that $x' = 2W$. The ratio $\frac{Kn}{400}$ is only a measure of the hydration rate of the cement compared with a certain standard, so that, with another constant according to a different test method, the formula of Graf is the same as ours.

It will be noted that all the formulæ give the strength of a mortar or concrete after a certain time, in other words for these cases we have to consider h as a constant and we might then substitute W as abscissæ for V_0. The curve may, between the abscissæ 50 and 20 per cent., which are the most used mixes, be drawn with a great approximation as a hyperbola of the form

$$F = \frac{E}{x} + D$$

or $\qquad F = E . \frac{c}{W} + D$ which is the formula of Lys.

Heat of Hydration of Cement and its Constituents.—III.

By O. F. HONUS

The Relation of the Heat of Hydration to the Physical Properties of Portland Cements.

THE purpose of the investigation is to determine whether there is any relationship between the heat of hydration and the compressive strength of commercial Portland cements. To this end seven selected cements have been tested at the Silicate Industries Institute, Brünn, by O. Kallauner and his colleagues.[142] The rational composition of these cements has been calculated and determined

Fig. 4.

graphically by the methods described in a previous paper.[143] In addition, three cements purchased through the usual trade channels have been included. These were tested by the writer, and their free-lime contents were determined. The chemical composition and the physical properties of these eleven cements are given in Table III and the rational composition in Table IV. In Fig. 4 the com-
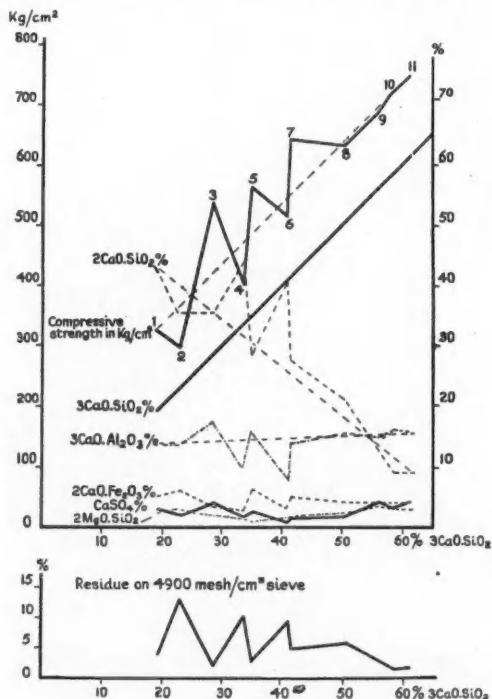
TABLE III.

CHEMICAL COMPOSITION AND PHYSICAL CONSTANTS.

Cement No.	1.	2.	3.*	4.*	5.	6.	7.	8.	9.*	10.	11.
Per cent. CO_2 ...	4·76	6·92	2·52	1·39	4·41	1·40	3·94	0·75	1·05	1·16	0·95
,, Free SiO_2	1·19	1·23	0·38	0·29	0·52	0·25	0·25	0·25	0·45	0·36	0·36
,, Combined SiO_2 ...	21·22	19·71	20·53	24·72	19·24	25·92	21·18	22·23	20·93	20·96	20·63
,, Al_2O_3 ...	5·19	5·09	6·44	3·73	6·50	3·29	5·23	5·91	5·66	6·04	5·90
,, Fe_2O_3 ...	3·05	3·47	2·03	1·89	3·54	1·92	2·91	2·49	2·48	2·41	2·31
,, CaO free...	n.t.	n.t.	3·92	3·27	n.t.	n.t.	n.t.	n.t.	1·33	n.t.	n.t.
,, CaO combined ...	n.t.	n.t.	60·54	63·28	n.t.	n.t.	n.t.	n.t.	64·08	n.t.	n.t.
,, Σ CaO ...	60·34	60·60	64·46	66·55	63·90	66·04	64·58	65·68	65·41	65·56	65·20
,, MgO ...	1·34	1·64	1·05	0·80	0·31	0·95	0·96	1·32	1·95	1·73	1·64
,, SO_3 ...	1·70	1·18	2·28	0·93	1·56	0·61	0·88	1·28	1·28	2·24	2·42
Total ...	98·79	99·81	99·68	100·30	99·98	100·38	99·93	99·91	100·17	100·16	99·41
Hydraulic modulus	2·00	2·10	2·20	2·18	2·18	2·10	2·20	2·14	2·25	2·23	2·26
Silicate modulus ...	2·58	2·30	2·40	4·40	1·92	4·98	2·60	2·65	2·57	2·48	2·54
Residue on the 4,900 mesh/cm² Sieve ...	2·80	13·00	2·27	10·00	2·80	9·61	5·00	6·00	2·50	1·40	1·60
Compressive strength in kg/cm² after 28 days combined storage ...	330	300	535	403	564	514	640	629	684	718	746
Weight per litre (loose) in g. ...	1010	990	1035	1115	920	1080	1085	1105	1032	—	1026
Gauging water for 1 : 3 mortar in per cent. ...	8·00	8·25	8·40	8·00	8·00	8·00	8·20	8·00	8·00	8·25	8·00

* Cements purchased in the open market.

TABLE IV.

Cement No.	1.	2.	3.	4.	5.	6.	7.	8.	9.	10.	11.
Per cent. $CaCO_3$ ...	10·82	15·73	5·70	3·16	10·20	3·18	8·95	1·70	2·39	2·63	2·16
,, SiO_2 free...	1·19	1·23	0·38	0·29	0·52	0·25	0·25	0·25	0·45	0·36	0·36
,, $2CaO.Fe_2O_3$	5·16	5·90	3·45	3·23	6·01	3·26	4·90	4·23	4·21	4·07	3·93
,, $3CaO.Al_2O_3$	13·70	13·50	17·04	9·86	16·21	8·65	13·80	15·64	14·98	16·00	15·60
,, $2CaO.SiO_2$	43·50	35·60	35·42	43·45	28·27	41·36	27·60	21·67	13·57	12·10	9·25
,, $3CaO.SiO_2$	19·00	22·80	28·06	34·06	34·74	40·80	41·10	50·60	56·00	58·50	61·40
,, $2MgO.SiO_2$	2·34	2·87	1·84	1·40	1·21	1·67	1·68	2·31	3·41	3·20	2·87
,, $CaSO_4$ ...	2·98	2·01	3·87	1·58	2·65	1·03	1·50	2·17	3·80	3·27	4·10
,, CaO free...	—	—	3·81	3·27	—	—	—	—	1·36	—	—
Total ...	98·69	99·64	99·57	100·30	99·81	100·20	99·78	98·57	100·17	100·13	99·67

pressive strengths of the cements have been plotted against tricalcium silicate contents so that the latter lie along a straight line ; the percentages of $2CaO.SiO_2$, $3CaO.Al_2O_3$, $2CaO.Fe_2O_3$, $CaSO_4$ and $2MgO.SiO_2$ are also shown, while the residues on a sieve with 4,900 meshes per square centimetre are given at the foot of the diagram.

INTERPRETATION OF THE CURVES IN FIG. 4.—It will be seen that there is neither practical nor theoretical relationship between tricalcium silicate content and strength. It is, however, clear that the dicalcium silicate content decreases as the tricalcium silicate content increases. If a hypothetical boundary line is drawn from Cement No. 1 to Cement No. 11 it will be found that the values for the dicalcium silicate content lie partly above and partly below this line (see Cements Nos. 2, 5 and 10 as compared with Nos. 4, 6, 7 and 8). The same applies to the tricalcium aluminate, the second of the hydraulic constituents in importance, although there may be some doubt whether it is permissible in this case to draw even a hypothetical boundary line. It would therefore seem that the varying contents of disilicate and tri-aluminate may sometimes enhance and

sometimes diminish the hydraulic properties of the cement. The greatest influence upon compressive strength appears to be exerted by the tricalcium silicate content expressed as a function of the sieve residue. In this connection reference must be made to the work of Carlson and Bates,[144] who found that the greater reactivity of the finest particles is to be attributed to their relatively higher tricalcium silicate content than to their greater surface area. The coarser particles
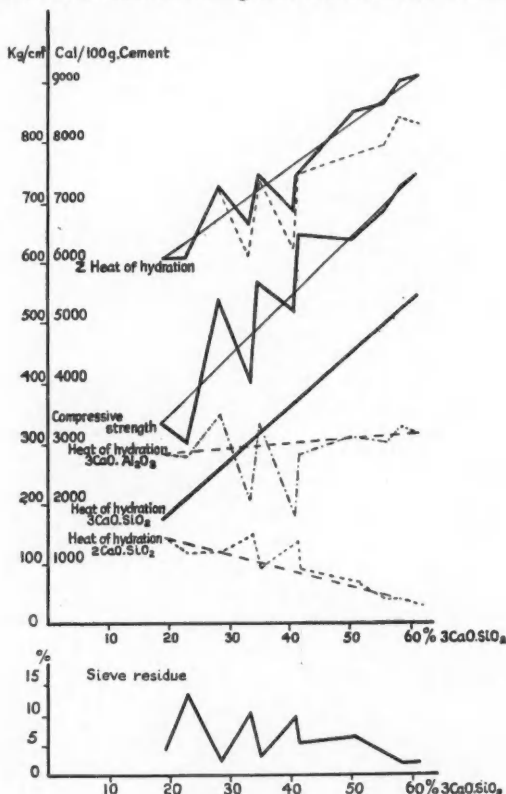
Fig. 5.

have a higher dicalcium silicate content. As a rational criterion for the fineness of Portland cement, Read-Lewis[145] assumes that the reactive surface and consequently the compressive strength increase with fineness in a measure governed by a coefficient given by the percentage contents of various sieve fractions. This theory has been accepted by a large number of concrete engineers but has found considerable opposition amongst chemists.

It is evident that in the cases of Cements Nos. 2, 4, 6 and 8 an increase of particle size is associated with a lower compressive strength. On the other hand,

the values for Cements Nos. 3, 5, 7, 9, 10 and 11 show that greater fineness or higher tricalcium silicate content with a given fineness are accompanied by higher compressive strength.

In order to discover what influence the heat of hydration has upon strength it was necessary to calculate the total heats of hydration from the values determined for the individual calcium compounds. The quantities of heat liberated by the hydration of the various compounds and the total quantities set free by the hydration of the cements are given in Table V, while Fig. 5 shows the relationships between total heat of hydration and the heats of hydration of the compounds and the strengths and sieve residues of the cements. The heat of hydration of the free lime has been neglected as it is probably without influence upon the strength development of the cement.

INTERPRETATION OF THE CURVES IN FIG. 5.—When the total heat of hydration is plotted against strength the curves are nearly parallel and indicate a close relationship. In the case of Cement No. 2 a small increase of total heat of hydration attributable entirely to $3CaO.SiO_2$ is associated with lower heats of hydration for $3CaO.Al_2O_3$ and $2CaO.SiO_2$. Nevertheless, this cement gives a lower strength than Cement No. 1, probably due to the fact that Cement No. 2 gives a relatively high residue on the sieve and may thus hydrate very slowly. The conclusion reached by Werk and Lasseter[146] that fine cements give high early strengths therefore holds good in the case of Cement No. 1 compared with No. 2. But it is not impossible that at a later date the strength of Cement No. 2 will exceed that of No. 1, for, as will be shown later, it is possible that hydration will be completed in time. Inadequate strength development is not, however, always caused by a large sieve residue and the slow hydration associated with it ; it may happen that with very fine cements rapid but incomplete hydration and

TABLE V.

HEAT OF HYDRATION IN CAL. FOR THE PERCENTAGE CONTENTS OF THE COMPOUNDS FOUND BY RATIONAL
ANALYSIS AND FOR 100G. CEMENT.

Cement No.		1.	2.	3.	4.	5.	6.	7.	8.	9.	10.	11.
$2CaO.Fe_2O_3$	...	36	41	24	22	42	22	34	29	29	28	27
$3CaO.Al_2O_3$...	...	2781	2740	3459	2001	3290	1755	2801	3174	3041	3248	3166
$2CaO.SiO_2$ ...	...	1435	1175	1170	1430	933	1365	911	715	449	399	305
$3CaO.SiO_2$ ...	...	1691	2029	2495	3080	3092	3631	3658	4503	4990	5206	5464
$CaSO_4$ ...	...	95	64	123	51	85	33	48	69	121	104	131
		6038	6049	7271	6584	7442	6806	7452	8490	8630	8985	9093
$2MgO.SiO_2$...	...	−16	−20	−12	−9	−8	−11	−11	−16	−23	−22	−20
CaO free ...	...			+1013	+870					+362		
Total	...	6022	6029	8272	7445	7434	6795	7441	8474	8969	8963	9073

loss of strength may be brought about by a deficiency of mixing water. The subject of incomplete hydration due to an insufficiency of mixing water will be dealt with later. Cement No. 3 displays higher strength associated with a higher total heat of hydration and a much lower sieve residue. Although Cement No. 4 has a higher tricalcium silicate content, its total heat of hydration is lower and is associated with a lower strength and a lower tricalcium aluminate content. The dicalcium silicate content is above the boundary line, and this compound

may be regarded as a diluent.   But here again the main point is the coarseness of the cement as revealed by the high sieve residue, and this is to a greater extent responsible for the loss of strength than is the high dicalcium silicate content.   The case of Cement No. 5 is very similar to that of No. 3.   Heat of hydration and strength are higher and sieve residue is lower.   In this case increased strength is to be attributed to the higher tricalcium silicate content and to the favourable influence of the greater tricalcium aluminate content.   Cement No. 6 exhibits lower heat of hydration, lower strength, higher sieve residue, higher dicalcium silicate content, and lower tricalcium aluminate content.   Nevertheless the strength is very near to the theoretical value.   Cement No. 7, like Nos. 3 and 5, displays higher tricalcium silicate content, higher heat of hydration, and higher strength associated with a lower sieve residue.   Cement No. 8 has a higher tricalcium silicate content, higher heat of hydration, and a slightly higher sieve residue, but gives a somewhat lower strength than Cement No. 7.   Cements Nos. 9, 10 and 11 exhibit increases in heat of hydration and strength that fall within the limits and an almost corresponding decrease in sieve residue.

It was now necessary to ascertain whether insufficient hydration could be the cause of the low strengths.   The investigation was based upon the following
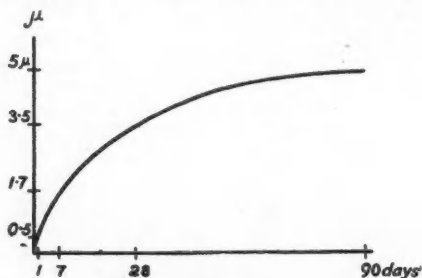
Fig. 6.

considerations.   (1) The energy content of a chemical compound is always the same regardless of whether its physical state is " coarse " or " fine."   (2) Provided the theoretical amount of water is available, the quantity of heat evolved when a cement reacts with water, or hydrates, will also be constant whether the cement be coarse or fine.   (3) If less than the theoretical quantity of water is available, the heat evolved on hydration will always be less no matter whether the cement is coarse or fine.   (4) In the process of hydration, the reaction velocity depends upon the proportion of mixing water and the rational composition and particle size of the cement.   (5) Therefore, if sufficient water is available and the cement is finely ground, hydration will be both rapid and complete.   (6) If the water is sufficient but the grinding not so fine complete hydration may be expected, but, owing to the smaller surface available for the reaction, it will proceed slowly.   (7) Insufficient water, whether the cement be coarse or fine, will be associated with incomplete hydration, failure to evolve the maximum heat of hydration, and impairment of the hydraulic properties.

The fineness of a cement cannot therefore constitute a criterion for its latent energy and hydraulic properties ; but it may exert a great influence upon the course of the reactions involved in hydration, which will proceed more rapidly with the finer cements and more slowly with the coarser cements. In this connection mention may be made of the work of Anderegg and Hubbel,[147] who found hydration to have proceeded to a depth of 0.5μ after twenty-four hours, 1.7μ after seven days, 3.5μ after twenty-eight days and 5.0μ after ninety days, and point out that the depth to which hydration extends is still greater with rapid-hardening cements. The progress of hydration with time is shown graphically in Fig. 6. Kühl[148] has confirmed these results for Portland cement and given the depth of hydration for high alumina cement as 0.4μ in one hour and 5.0μ in twenty-four hours. These results taken together indicate an intimate relationship between the depth to which hydration proceeds and the rate at which strength is developed.

In order to ascertain whether hydration had been incomplete with the cements investigated, it was necessary to calculate the theoretical quantity of water required for complete hydration. For this purpose it was assumed that the hydration products postulated are actually formed ; and the calculation was based upon the following values :

1 g. $2CaO.Fe_2O_3$	..	..	..	.. 0.3309 g. water
1 g. $3CaO.Al_2O_3$	..	..	..	.. 0.4000 ,,
1 g. CaO (free) ..	..	..	..	.. 0.3210 ,,
1 g. $2CaO.SiO_2$ ..	..	..	..	.. 0.3660 ,,
1 g. $3CaO.SiO_2$ ..	..	..	..	.. 0.3550 ,,
1 g. $2MgO.SiO_2$ ..	..	..	..	.. 0.4500 ,,
1 g. $CaSO_4.0.5H_2O$	..	..	..	.. 0.1990 ,,

No scientific basis has yet been found for determining the water requirements of cements or their mixtures with sand ; both science and practice still cling to the purely empirical rules that have been devised, and which still suffice for present-day conditions. The difficulties of the problem are at once evident if it be assumed, in agreement with Giertz-Hedström,[149] that water can be present in the system cement-sand-water in three different states, namely, firmly-held, loosely-held, and free. Firmly-held water is defined as that which remains in a finely sub-divided sample after rapid isothermal drying, and comprises strongly adsorbed water in addition to chemically combined water—water of hydration and water of crystallisation. Loosely-held water is defined as water that cannot be removed by freezing, and includes capillary and weakly adsorbed water. Free water is that which can be removed from the system by freezing. The water absorption of cement is liable to great fluctuations which, however, are subject to certain limitations as recently demonstrated by the work of Hänsel, Steinherz and Wagner.[150] In practice the water requirements of cement-sand mixes are determined by purely empirical rules, such as that of Davey.[151]

In Table VI are given the theoretical water requirements of the cements, which are shown for the various cement constituents, for each cement, and for a 1 : 3 standard sand mix of each, and the experimentally determined values. The probable extent of hydration has been calculated from these experimental and theoretical values and expressed as a percentage. It will be seen from Table VI that the conditions for a 100 per cent. or nearly 100 per cent. hydration existed
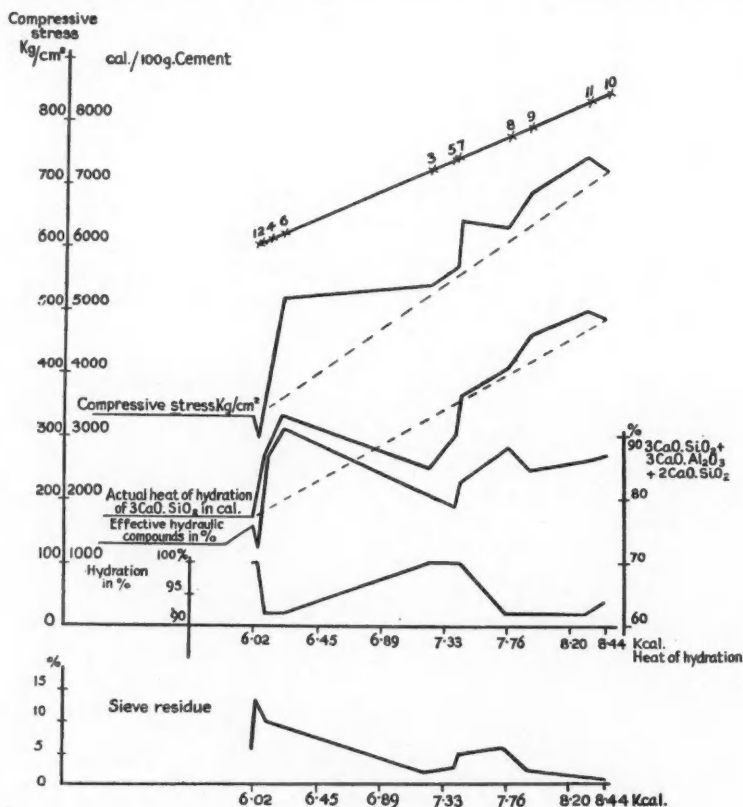
Fig. 7.

in the cases of Cements Nos. 1, 2, 3, 5 and 7 as soon as the fineness of the cement had attained a certain maximum value. When particle size is larger hydration may proceed to completion, though more slowly, unless prevented by other factors ; in either case this would be reflected in the rate at which strength is developed. The extent of hydration is about 92 per cent. for Cements Nos. 4, 6, 8, 9 and 11 and about 94 per cent. for No. 10.

TABLE VI.

THEORETICAL WATER REQUIREMENTS OF 100G. CEMENT AND OF A 1 : 3 MORTAR.

Cement No.	1.	2.	3.	4.	5.	6.	7.	8.	9.	10.	11.
$2CaO.Fe_2O_3$ ...	1·71	1·95	1·14	1·07	1·99	1·08	1·62	1·40	1·39	1·35	1·30
$3CaO.Al_2O_3$ ...	5·48	5·40	6·81	3·94	6·48	3·46	5·52	6·25	5·99	6·40	6·24
$2CaO.SiO_2$ ...	15·92	13·03	12·96	15·90	10·35	15·14	10·10	7·93	4·97	4·42	3·38
$3CaO.SiO_2$ ...	6·75	8·09	9·96	12·09	12·33	14·48	14·59	17·96	19·88	20·77	21·80
$2MgO.SiO_2$ ...	1·05	1·29	0·83	0·63	0·54	0·75	0·75	1·04	1·53	1·44	1·29
$CaSO_4.O.5H_2O$ ...	0·59	0·40	0·77	0·31	0·53	0·20	0·30	0·43	0·76	0·65	0·82
CaO free	—	—	1·22	1·05	—	—	—	—	0·44	—	—
Total ...	31·50	30·16	33·69	34·99	32·22	35·11	32·88	35·01	34·96	35·03	34·83
For a 1 : 3 mortar...	7·88	7·54	8·42	8·75	8·05	8·78	8·22	8·75	8·74	8·76	8·71
Measured water requirement ...	8·00	8·25	8·40	8·00	8·00	8·00	·8·20	8·00	8·00	8·25	8·00
Hydration, per cent.	100	100	99·77	91·43	99·38	91·12	99·76	91·43	91·54	94·18	91·85

In Table VII are given the total quantities of heat evolved during the hydration of the cements ; this is also shown by the dotted line in Fig. 5.

It is now possible to draw certain conclusions. For instance, with Cements Nos. 4 and 6 hydration was incomplete, and this, as well as the relative coarseness of the cement, has not been without influence upon the strength developed. On the other hand, Cements Nos. 3 and 5 were completely hydrated ; they are very finely ground and have dicalcium silicate contents a little below the limiting value, while their tricalcium aluminate contents are somewhat higher than the limit. This is to be regarded as the reason why their strengths are higher than would be expected of a normal cement.

As a matter of interest an attempt has been made to correlate the quantities of tricalcium silicate and of cement actually hydrated with the values obtained for compressive strength in order to discover whether the tricalcium silicate content is indeed the factor that has the greatest influence on strength. The results are shown in Fig. 7, in which the cements have been arranged in ascending order according to their heats of hydration and are represented by the straight line at the top of the diagram. Beneath this is the strength curve; then the quantity of heat liberated by the hydration of the tricalcium silicate, the values for which are given in Table VIII ; further, the extent of hydration expressed as a percentage, and finally the sieve residue.

INTERPRETATION OF FIG. 7.—In general Fig 7 shows that the tricalcium silicate content, indicated by the heat of hydration, has the greatest influence upon the strength developed by the cement. This is demonstrated by the similarity of the curves for strength and heat of hydration of tricalcium silicate. It will also be seen that Cements Nos. 3 and 5 give higher strengths than Nos. 4 and 6 in spite of their low tricalcium silicate contents. The reason for this is to be found in the values for the sieve residue, which in the case of Cements Nos. 3 and 5 do not exceed 3 per cent. but for Nos. 4 and 6 are about 10 per cent. Another reason, intimately connected with that already mentioned, is the percentage hydration, which for Cements Nos. 3 and 5 is almost 100 per cent. but for Nos. 4 and 6 only attain the theoretical minimum of 92 per cent. In the case of Cement No. 2 it is probable that the high sieve residue is the sole cause of the

inadequate hydration, unless an error has been introduced by the presence of free lime that has not been taken into account in the calculations; this would agree well with the work of Steinour and Woods[152] who found a loss of strength with increasing free lime content.   In spite of a higher value for the heat of hydration of tricalcium silicate, Cement No. 8 has a crushing strength about 10 kg. per square centimetre less than Cement No. 7.   Here again incomplete hydration and higher sieve residue are the cause of lower strength.   The behaviour of Cements Nos. 9, 10 and 11 is normal.

TABLE VII.

TOTAL HEAT OF HYDRATION IN CAL/100G.

Cements in order of percentage hydration.

Cement No.	1.	2.	4.	6.	3.	5.	7.	8.	9.	11.	10.
	6022	6029	6030	6190	7242	7389	7422	7745	7880	8330	8440

TABLE VIII.

HEAT OF HYDRATION OF THE TRICALCIUM SILICATE IN CAL.
Cements in order of percentage hydration.

Cement No.	1.	2.	4.	6.	3.	5.	7.	8.	9.	11.	10.
	1691	2029	2815	3307	2489	3073	3649	4115	4566	5018	4900

TABLE IX.

THE PROPORTIONS OF THE MOST EFFECTIVE HYDRAULIC COMPOUNDS.
$3CaO.SiO_2 + 3CaO.Al_2O_3 + 2CaO.SiO_2$ in per cent.

Cement No.	1.	2.	4.	6.	3.	5.	7.	8.	9.	11.	10.
	76·2	71·9	87·4	90·8	80·5	79·2	82·5	87·9	84·5	86·3	86·6

In order to see how the proportions of the most effective hydraulic compounds in the various cements compared with strength and heat of hydration, the sums of the contents of tricalcium silicate, tricalcium aluminate and dicalcium silicate have been plotted in Fig. 7.   When an endeavour is made to interpret the curve thus obtained the conviction is gained that in the case of Cement No. 2 the small content of the major hydraulic compounds is to be associated with the high sieve residue as being responsible for the low strength.   With Cement No. 5, the 6 per cent. higher tricalcium silicate content outweighs the 1 per cent. higher sieve residue and the 1·5 per cent. lower content of major hydraulic compounds, and as a result the cement is able to develop still higher strength than Cement No. 3. In the case of Cement No. 8 the lower strength seems to be due rather to the assumption that free lime must be present (although not detected) than to the higher sieve residue.[152]   In such cases the rational analysis is not entirely reliable.

It will be realised from the foregoing that quite superficial observations lead to a maze of unsolved problems which nevertheless may be solved by patient and persistent research.   The rises in temperature that may occur during the hydration of these cements will form the subject of a further paper.

SUMMARY.

A brief résumé of the present state of knowledge regarding the hydration of the compounds comprised in the ternary system $CaO.Al_2O_3.SiO_2$ is followed by

an examination of the relationships that exist between the physical properties of commercial Portland cements and their heats of hydration. For this purpose the heats of hydration were calculated from the thermochemical formulæ for the heats of solution of the various compounds.

Although it is probable that perfectly reliable results can only be obtained from experiments with cements at ages of six or more months, valuable information has been yielded by the examination of data for the heat evolved and strength developed in twenty-eight days.

The results of the investigation may be summarised as follows :

(1) An increase in the tricalcium silicate content of a cement is not necessarily always accompanied by a rise in strength. Although strength development is influenced to a considerable extent by the tricalcium silicate content it is mainly dependent upon first the fineness of grinding and second the extent of hydration, which again depends upon the amount of water available and the fineness of the cement.

(2) The curves for strength and total heat of hydration are nearly parallel, and both are strongly influenced by variations in the tricalcium aluminate and dicalcium silicate contents.

(3) A small sieve residue is not always associated with high strength, especially when the cement has a very low tricalcium silicate content.

(4) It is shown that the tricalcium silicate content of a cement can influence its strength to a very great extent no matter whether the cement is coarse or fine, or hydration complete or not. In these cases the heat-of-hydration curve is nearly parallel to the strength curve.

(5) The factor that governs the development of strength is the particle size of the principal hydraulic compounds. It may be expected that, given uniform particle size and complete hydration of the cement, increase in tricalcium silicate content will always lead to higher strengths.

(6) In determining the rational composition of a cement particular attention must be paid to the presence of free lime or the rational analysis will lead to erroneous conclusions.

(Concluded)

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Studies on Italian Pozzolana and Pozzolanic Portland Cement.

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THE object of the present study is to compare Italian and Japanese pozzolanas and pozzolanic Portland cements. Six samples of Italian pozzolanic Portland cements were analysed ; the results are given in Table I.

TABLE I.

CHEMICAL COMPOSITION OF ITALIAN POZZOLANIC PORTLAND CEMENTS.

Sample.	Loss on ignition.	Insoluble residue.	Total. SiO_2.	Total Al_2O_3.	Total Fe_2O_3.	Total CaO.	Total MgO.	Total SO_3.
No.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
8	1.89	5.10	36.89	5.42	10.25	41.41	1.27	1.03
9	4.04	20.54	24.29	12.09	6.97	48.26	0.31	2.37
10	3.49	3.36	21.05	12.22	9.59	50.21	trace	1.45
11	5.88	6.07	33.97	5.97	10.23	40.91	,,	2.09
12	4.09	12.57	31.26	7.33	10.84	45.01	,,	1.31
13	4.76	12.77	38.71	4.47	2.71	45.73	,,	2.10

TABLE II.

Sample.	Cement.	Loss on ignition	Insoluble residue	SiO_2	Al_2O_3	Fe_2O_3	Mn_2O_3	CaO	MgO	SO_3
No.		Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.
7	Blast furnace slag cement	0.13	0.39	25.59	11.11	4.53	3.18	50.45	2.68	2.15
14	,, ,,	−0.52	1.02	26.17	8.12	3.40	2.12	56.23	2.58	1.84
15	,, ,,	−0.49	2.09	27.08	10.70	3.16	1.06	55.61	1.71	1.75
16	Neo-soliditite cement ...	1.60	16.68	32.33	5.28	3.97	—	52.44	0.88	1.74
6	Portland cement ...	0.78	0.16	22.37	6.15	2.88	—	64.60	1.36	1.24

TABLE III.

RESULTS OF COMPRESSION TESTS.

Sample.	Cement.	Water-cement ratio.	Compressive Strength (Days) (kg/cm^2).		
			3	7	28
No.		Per cent.			
8	Italian Pozzolanic Portland cement	68	80	120	143
9	,, ,, ,, ,, ...	68	38	74	164
10	,, ,, ,, ,, ...	68	65	95	177
11	,, ,, ,, ,, ...	70	25	53	112
12	,, ,, ,, ,, ...	70	24	55	153
13	,, ,, ,, ,, ...	70	40	112	213
7	Japanese Blast furnace slag cement	65	75	135	296
14	,, ,, ,, ,, ,, ...	60	92	143	272
15	,, ,, ,, ,, ,, ...	60	67	129	273
16	Neo-soliditite cement	65	103	143	223
6	Japanese Portland cement	65	57	113	233

Five Japanese cement samples were used for comparison, as follows : Three blastfurnace slag cements, two of which were prepared in the laboratory by mixing and grinding blastfurnace slag with Portland cement or its clinker ; one neosoliditite cement (produced by mixing and grinding Portland cement clinker, ignited granite, and natural siliceous earth) ; and one Portland cement. The chemical compositions are given in Table II.

Using cylindrical test pieces 2 cm. diameter by 3 cm. long, composed of 1 : 3 cement-standard sand mortar of high water-cement ratio, or so-called plastic or wet mortar, the results given in Table II were obtained.

Three Italian pozzolanas, two Japanese pozzolanas, one siliceous earth (Keisan-Hakudo), one spent shale, and two blastfurnace slags were compared on chemical composition, etc. The results are given in Table IV.

TABLE IV.

CHEMICAL COMPOSITION.

Sample.	Sample.	Loss on ignition.	Insoluble residue	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	SO_3
No.		Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	Per cent.	
38	Italian pozzolana	8.48	17.19	45.15	17.02	11.42	10.00	2.12	Trace
39	,, ,,	6.30	62.32	52.81	18.63	10.19	7.54	Trace	,,
40	,, ,,	7.68	33.37	47.37	14.13	15.94	9.12	,,	,,
30	Japanese pozzolana	11.48	46.59	38.70	26.74	20.40	0.70	0.78	0.64
43	,, ,,	10.95	48.10	43.03	24.65	19.35	1.05	0.69	Trace
32	Siliceous earth ..	9.66	77.15	68.78	13.60	3.50	1.69	1.19	0.52
26	Spent shale......	1.06	85.75	61.76	22.01	10.39	2.42	1.32	0.78
23	Blastfurnace slag .	−1.12	1.40	32.51	15.52	1.38	43.59	3.05	2.42
25	,, ,, ,, .	−0.81	0.63	42.73	8.12	1.01	43.12	1.55	1.04

TABLE V.

Sample.	Cement.	Water-cement-ratio.	Compressive Strength (kg/cm²).		
			3 days.	7 days.	28 days.
No.		Per cent.			
1	Portland cement	60	97.2	177.2	263.0
44	Pozzolanic Portland cement	60	85.6	108.2	244.2
45	,, ,, ,, ...	60	77.5	105.8	163.0
46	,, ,, ,, ...	60	76.6	118.6	223.0
47	,, ,, ,, ...	60	44.1	89.2	167.6
48	,, ,, ,, ...	60	40.0	84.5	153.9
40	Siliceous earth Portland cement..	60	81.0	142.3	251.3
50	Spent shale Portland cement	65	66.2	107.8	200.6
51	Blastfurnace slag cement	60	95.1	184.4	336.0
52	Pozzolanic lime cement	70	—	17.6	42.4
53	,, ,, ,, ...	65	—	4.6	29.6
54	,, ,, ,, ...	65	—	24.9	78.8
55	,, ,, ,, ...	65	—	24.6	61.0
56	,, ,, ,, ...	70	—	11.5	44.4
57	Siliceous earth lime cement	70	—	6.1	50.2
58	Spent shale lime cement	70	—	1.9	9.4
59	Slag cement	60	—	83.9	126.6
67	,, ,, ...	60	—	7.4	29.4

TABLE VI.

S'ple No.		Proportions. Portland cement or slaked lime.	Pozzolanic material.	Fineness 4900M/cm² Sieve residue. Per cent.	Loss on Ignition. Per cent.	Insoluble residue. Per cent.	SiO₂ Per cent.	Al₂O₃ Per cent.	Fe₂O₃ Per cent.	CaO Per cent.	MgO Per cent.	SO₃ Per cent.	Free lime. Per cent.
1	Portland cement	Cement 100	—	2.8	1.14	0.26	21.50	5.51	2.80	65.12	1.69	1.41	1.37
44	Pozzolanic Portland cement	60	Italian pozzolana No. 38 40	2.0	3.81	7.12	31.20	10.11	6.31	44.64	0.97	0.67	0.76
45	,, ,,	60	,, 39 40	0.2	2.09	25.52	36.97	10.54	5.28	40.94	0.59	1.06	0.74
46	,, ,,	60	,, 40 40	0.8	3.64	13.46	32.63	9.55	7.67	42.40	0.79	0.92	0.56
47	,, ,,	60	Japanese pozzolana 30 40	4.4	5.32	18.33	28.93	13.78	10.54	39.16	0.81	0.87	0.74
48	,, ,,	60	,, 43 40	3.6	4.02	18.64	30.32	13.43	10.66	39.61	0.86	0.70	0.59
49	Siliceous earth ,,	60	Siliceous earth 32 40	0.4	4.13	31.54	39.64	10.32	3.43	39.44	1.21	1.03	0.43
50	Spent shale ,,	60	Spent shale 26 40	1.4	1.12	33.86	37.50	12.13	6.50	39.56	1.28	1.20	0.59
51	Blastfurnace slag cement	60	Blastfurnace slag 23 40	0.4	0.73	1.31	26.01	9.41	2.44	56.00	2.12	1.39	0.81
66	,, ,, ,,	60	,, 25 40	3.0	-0.22	2.01	29.32	7.45	2.54	54.71	1.38	1.01	0.75
52	Pozzolanic lime cement	Lime 30	Italian Pozzolana No. 38 70	8.6	13.28	14.06	32.05	11.06	8.15	30.15	1.78	Tr	15.91
53	,, ,, ,,	30	,, 39 70	0.2	11.34	45.83	38.97	12.91	5.68	27.29	Tr	Tr	16.19
54	,, ,, ,,	30	,, 40 70	2.2	12.49	24.65	33.76	10.95	9.50	28.36	Tr	Tr	16.19
55	,, ,, ,,	30	Japanese pozzolana 30 70	16.0	15.71	30.30	28.10	18.55	14.04	21.82	0.68	0.61	14.94
56	,, ,, ,,	30	,, 43 70	19.0	14.64	31.61	29.78	17.52	13.42	22.88	0.66	Tr	15.71
57	Siliceous earth lime cement	30	Siliceous earth 32 70	8.0	13.35	54.50	49.51	9.26	3.43	22.91	0.92	0.31	16.21
58	Spent shale lime cement	30	Spent shale 26 70	4.8	8.09	61.76	43.23	16.57	8.30	22.04	0.81	0.73	16.36
59	Slag cement	30	Blastfurnace slag 23 70	0.6	7.25	1.12	22.23	10.18	1.22	53.69	1.52	1.42	18.41
67	,, ,,	30	,, 25 70	9.4	6.81	0.34	29.54	5.26	0.80	53.25	1.31	0.97	17.77

These pozzolanic materials were mixed and ground with Portland cement ; the resulting physical properties and chemical compositions were as shown in Table VI. The samples of pozzolanic Portland cement and pozzolanic lime cement were tested on small cylindrical test pieces, using 1 : 3 cement-sand mortar of high water-cement-ratio (0.60 to 0.70) ; the results are given in Table V.

The pozzolanic materials were also mixed with slaked lime and ground intimately to make pozzolanic lime cement ; the resulting physical properties and chemical compositions are shown in Table VI.

It was observed that pozzolanic Portland cements have less expansion than pozzolanic lime cements.

Cement Mortars Impregnated in Sulphur.

DR. ING. Georg Sänger describes investigations on the changes in cement mortar after impregnation in sulphur baths (*Zement*, 39/1933) ; reference is made to publications by Kabbé in *Engineering News-Record*, Bates in *Industrial and Engineering Chemistry*, and by Obst and Ferd. Richter in *Zement* (1927).

The author states that United States experience has shown considerable increase in the compression strengths of concrete treated with sulphur. The present investigations were limited to 1 : 3, 1 : 5 and 1 : 8 mortars, made of two different Portland cements and one blastfurnace Portland cement. Variations in time and temperature of the sulphur baths were investigated with reference to their influence on compression strength, abrasion, and resistance to chemical attacks.

Dr. Sänger's investigations showed that, contrary to United States experience, mortars can be impregnated only very slowly except in the case of lean mixtures. Melted sulphur of 130 deg. to 150 deg. C. penetrates about 1 mm. in one hour in the case of mortars prepared moist. The rate of impregnation increased when the mortar was immersed in baths at 160 deg. to 170 deg. C. and afterwards at 125 deg. to 130 deg. C. The quantity of sulphur absorbed in the high-temperature bath was in many cases less than that absorbed in the same time in the lower temperature. Portland and blastfurnace Portland cement were about equal as regards speed of absorption of sulphur.

The increases of strength of concrete as recorded in the United States were experienced with cement mortars also. Saturation with sulphur increased strength very considerably, weak mixtures sometimes showing higher strengths than rich mixtures. Compression strengths of impregnated mortars were two to five times as high as those of unimpregnated mortars.

The compression strength was practically independent of the viscosity of the mortar as prepared. Abrasion was reduced considerably. Impregnation did not, however, prevent damage by chemicals, although destruction was very much slower.

Storage in water produced cracks after two years, whilst storage in open air and in a room caused no signs of deterioration to appear within this period. At longer periods mortar stored in open air would probably also show cracks. Impregnated mortars are therefore stated to be unsuitable for concrete work exposed to water or to the influence of the weather. Whether they could be used for structures not exposed to water or the influence of weather, would have to be ascertained by tests extending over longer periods.

Checking the Accuracy of Cement-Testing Sieves.

THE British Standard Specification for Portland Cement gives the maximum permissible variations in the sizes of the apertures and the diameters of the wires of testing sieves, and it is therefore necessary to check the accuracy of these dimensions. The Associated Portland Cement Manufacturers, Ltd., have recently set up an apparatus (supplied by Messrs. G. Cussons, Ltd., The Technical Works, Manchester) for this purpose, in which an image of the wire mesh magnified 100 times is projected on a ground-glass screen. It is then possible to measure the apertures and the wires in the projected image with screw dividers and an ordinary scale.
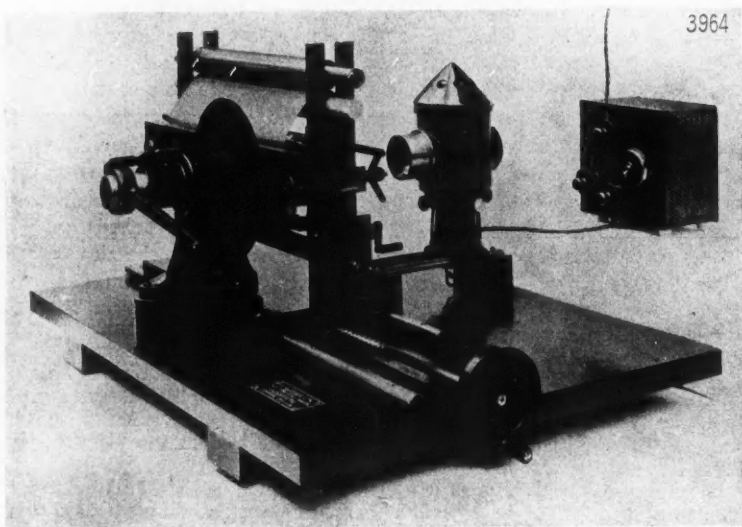
The tests can be made on pieces or on rolls of wire cloth. The usual procedure is to wind a roll of wire on a spindle, and by means of screw mechanisms it can be made to pass vertically or horizontally in front of the lens. Thus a systematic examination can be made of every part of the mesh and any irregularity of weaving and/or diameter or distortion of the mesh is easily detected on the screen. Measurements by a scale can then be made to ascertain whether the Specification limits have been exceeded.

The source of light for the projection is a Pointolite lamp, and a special lens system has been evolved which enables an accuracy of $\pm$ 0.01 in. to be guaranteed

within a circle of 2 ft. diameter at a magnification of 100 diameters, representing an accuracy of 0.0001 in. on the sieve. The screen is approximately 15 ft. distant from the lens, and cord connections enable an operator standing at the screen to focus the image.

To prevent distortion of a roll of wire, which is usually 1 ft. 6 in. wide and may be up to 50 ft. long, it is passed over a series of polished plated steel rollers. To enable a sharp image to be obtained the wire cloth passes between two strips of bevelled plate glass which can be clamped firmly together while taking the measurements.

Permeability as a Method of Investigation for Portland Cement Mortars.

In a recent number of *Zement*, Messrs. H. Kühl, J. Parga-Pondal, and S. Baentsch give an historical survey of the methods used for investigating the corrosion of cement, mortar and concrete, which has led to the development of a method of investigation which allows of following the processes occurring in mortar. The method consists in forcing water under pressure through porous mortar and analysing the liquid which passes through. The change of strength of the specimen is measured after the test. The tests were carried out on porous cylindrical specimens made from 1 part cement and 3 to 8 parts mixed sand. They were tested under moderate pressure after various periods of curing in water, air, and combined water and air.

In general, prolonged curing reduced permeability. In the case of specimens cured in water this was due to a swelling of the cement particles ; in the case of air-cured specimens it was due to carbonation and ageing of the cell walls. All specimens showed a tendency to become less porous shortly after commencing the test ; this was more marked in water-cured than in air-cured specimens. If the specimen is so porous that this effect does not appear, the permeability increases rapidly during the test. The test generally reduces the strength of the specimen, and the effect is more marked at early ages. Alkalis are leached out first, and the lime concentration of the water, which is greatest for water cured and least for air cured specimens, is subject to large variations. Alumina and iron oxide are not present in the leaching water ; the absence of the former is due to the formation of calcium sulphoaluminate. When the leaching water is rich in lime it is practically free from silica, but with low lime and high alkali concentration silica may be present. With high lime concentration the leaching water is practically free from SO_3 but with low lime concentration a high SO_3 content is obtained. The absence or presence of SO_3 is due to the formation or hydrolysis of calcium sulphoaluminate.

The investigation of the system Portland cement—water has led to the conclusion that this method of testing is also suitable for other systems, and work is proceeding in this direction.

INTERNATIONAL DICTIONARY OF CEMENT.

Arranged by Dr. C. R. Platzmann, with collaborators in England, France, and Spain.

(*Continued.*)

R

Spanish.	French.	English.	German.
reparación	réparation	repair	Reparatur
residuo	residu	residue	Rückstand
residuo insoluble	résidu insoluble	insoluble residue	unlöslicher Rückstand
resistencia	résistance	{ resistance	Widerstand (elektr.)
		{ strength	Festigkeit
resistencia a la compresión	résistance à la compression	compression strength	Druckfestigkeit
resistencia a la flexión	résistance à la flexion	bending strength	Biegefestigkeit
resistencia a la tracción	résistance à la traction	tensile strength	Zugfestigkeit
resorte o muelle	ressort	spring	Feder
retardador	retardateur	retarder	Abbindeverzögerer
revestimiento o forro del horno	garnissage du four	kiln lining	Ofenfutter
revista	journal, revue, coussinet	journal	Zeitschrift, Lager
revistimiento refractario del horno rotatorio	garnissage du four rotatif	rotary kiln lining	Drehofenfutter
revolución	rotation, révolution	revolution	Umdrehung
rodillos para los hornos	galet du four	roller for kiln	Ofenwalzlager
rozamiento	frottement	friction	Reibung
rueda	roue	wheel	Rad
rueda de oruga	chenille	caterpillar track	Raupenrad

S

Spanish.	French.	English.	German.
saco con válvula	sac à valvule	valve bag	Ventilsack
secador	séchoir	drier	Trockner
secador rotatorio	séchoir rotatif	{ drying drum	Trockentrommel
		{ rotary drier	Trommeltrockner
sección delgada	section mince	thin section	Dünnschliff
sección transversal	section transversale	cross section	Querschnitt
semiacero	fer coulé	semi-steel	Flusstahl
separador centrífugo	séparateur centrifuge	centrifugal separator	Zentrifugalabscheider
separador de aire	séparateur à air	air separator	Windsichter
separador de tipo de tambor	séparateur à tambour	drum type separator	Trommelabscheider
separación por aire	séparation par l'air	air separation	Windsichtung
silex (guijarro)	cailloux, silex	flint	Flintstein
sílice	silice	silica	Kieselsäure
silíceo	siliceux	siliceous	kieselsäurehaltig
silo	silo	bin	Behälter
silo de almacenaje	bassin d'attente	storage tank	Lagerbehälter
silo de mezcla	bassin à mélangeurs	mixing tank	Mischtank
sobrecarga	surcharge	overload	Ueberlastung
sobresaturado	sursaturé	supersaturated	übersättigt
sodio	sodium	sodium	Natrium
soldar	souder, suer	to weld	schweissen
solubilidad	solubilité	solubility	Löslichkeit
solución	solution, liqueur	solution	Lösung
soporte	chaise	pedestal	Lager, Lagerrahmen
soporte de rodillos	palier à rouleaux	roller bearing	Walzlager, Laufringlager
subenfriado	refroidi	super-cooled	unterkühlt
superficie	surface	surface	Oberfläche

T

tablero de fluidez	doseur à plateau	flow table	Fliesstisch
taller de reparación	atelier de reparation	repair shop	Reparaturwerkstätte
tamíz	tamis	{ screen	Sieb
		{ sieve	Sieb
tanto por ciento	proportion centésimale	percentage	Prozentgehalt
temple	trempe	tempering	Tempern
tensión del vapor	tension de la vapeur	vapour pressure	Dampftension
tensión superficial	tension superficielle	surface tension	Oberflächenspannung
termo-par	thermo-couple	thermo-couple	Thermoelement
tiempo de fraguado	temps de prise	setting-time	Abbindezeit
tipo de estrella triángulo	type étoile-triangle	star-delta type	Sterndreieckstyp (elektr.)
tiro forzado	tirage mécanique	induced draught	Saugzug
tolva	{ dévaloir	{ chute	{ Schütte
	{ trémie	{ hopper	{ Trichterbehälter
toma de tierra	mise à la terre	earthing	Erdung
tonelada	tonne	ton	Tonne
tornillo alimentador	vis alimentaire	feeding screw	Zufuhrschnecke
tornillo mezclador	vis mélangeuse	mixing screw	Mischschnecke
torno	tour	lathe	Drehbank
transmisión del calor	transmission de la chaleur	heat transmission	Wärmeübertragung
transmisión par correa	commande par courroie	belt drive	Riemenantrieb
transmisión por cables	commande par câbles	rope drive	Seilantrieb
transmisión por cadena	commande par chaîne	chain drive	Kettenantrieb
transportador aéreo de cable	{ transporteur aérien	{ cableway	Seilbahn
	{ funiculaire aérien	{ ropeway	
transportador de artesas	transporteur à augets	tray conveyor	Kastentransporteur
transportador de canales	convoyeur à bande en auget	troughed band conveyor	Förderrinne
transportador de cinta	convoyeur à bande	band conveyor	Bandtransporteur
transportador de cinta de acero	convoyeur à bande d'acier	steel band conveyor	Stahlbandtransporteur
transportador de correa	transporteur à courroie	belt conveyor	Bandtransporteur
transportador de impulsión	convoyeur rotatif, basculeur	swinging conveyor	Schwingtransporten
transportador de sacudidas	transporteur à secousses	shaker conveyor	Schütteltransporteur
transportador de sacudidas	transporteur à va-et-vient	shuttle conveyor	Schütteltransporteur
transportador de tornillo	viss transporteuse	screw conveyor	Schnecke, Sckraubentransporteur
transportador espiral ; transportador de tornillo	convoyeur à vis ; vis transporteuse	spiral conveyor	Transportschnecke
traviesa	anneau mortier	sleeper	Schwelle
triángulo de alambre	trépied en fer, triangle	wire triangle	Drahtdreieck
trípode	trépied	tripod	Dreifuss
trituradora	concasseur	crusher	Brecher
trituradora de discos	concasseur à cône oscillant	disc crusher	Scheibenbrecher
trituradora de martillos	broyeur à marteaux	hammer crusher	Hammerbrecher
triturador de noria	broyeur à meules	edge-runner	Kollergang
triturador de rodillo	broyeur à cylindres	roll crusher	Walzenbrecher
tubería	conduite	pipeline	Rohrleitung
tubería del mechero	tuyau du brûleur	burner pipe	Brennrohr
tubo	tube	tube	Rohr
tubo capilar	tube capillaire	capillary tube	Kapillarrohr
turbo generador	turbo-alternateur	turbo-generator	Turbogenerator
turno	poste, travail d'une équipe	shift	Arbeitschicht

V

vagoneta volquete	wagon à caisse basculante	tippler truck	Kippwagen
valoración	dosage	titration	Titration
valorar	titrer	titrate, to	titrieren
válvula	soupape, valvule	valve	Ventil
válvula corredera	tiroir	slide valve	Schiebeventil
válvula de cuello	vanne papillon	throttle valve	Winddrosselschieber
válvula fusible	coupe-circuit	fuse	Sicherung (elektr.)
vapor	vapeur	steam	Dampf
velocidad	vitesse	{ speed	Geschwindigkeit
		{ velocity	Geschwindigkeit
velocidad inicial	vitesse initiale	initial speed	Anfangsgeschwindigkeit
ventilador	ventilateur	fan	Ventilator
voladura	abattage à la poudre	blasting	Sprengung
volante	volant	fly-wheel	Schwungrad
volcador	basculeur	tippler	Kippvorrichtung
voltaje	tension	voltage	Spannung (elektr.)
via seca	procédé sec	dry process	Trockenverfahren

Y

yacimiento	dépôt	deposit	Lager, Vorkommen
yeso	gypse	gypsum	Gips
yeso de Paris	plâtre de Paris	plaster of Paris	Stuckgips

Z

zona de clinkerización	zone de cuisson	burning zone	Sinterzone

Trade Notices.

DATA ON HEATING AND VENTILATING.—A publication giving a great deal of useful data on the resistance of air ducts, equalisation of pipe diameters, weights of galvanised iron pipes and elbows, and other information of use to those concerned with heating and ventilation, together with friction and psychrometric charts, has been issued by Messrs. Davidson and Co., Ltd., Sirocco Engineering Works, Belfast.

CENTRIFUGAL PUMPS.—Messrs. Ruston and Hornsby, Ltd., of Lincoln, have issued a large and well-illustrated catalogue describing their range of centrifugal pumps, covering single and multi-stage pumps from 1 in. to 24 in. delivery branch diameter. The types include pumps suitable for clear water, sewage, solids or semi-solids in suspension, and water containing sand or other abrasive materials. A range of small ram pumps is also listed, and illustrations are given of small pumping plants driven by petrol-paraffin engines. The book concludes with useful information on pipelines, friction losses, etc., to enable gross total heads to be calculated.

INDEX TO ADVERTISERS.